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Transition-Metal-Free, Potassium *tert*-Butoxide/Dimethyl Sulfoxide Mediated Amination between Tertiary Amines and Aryl Halides

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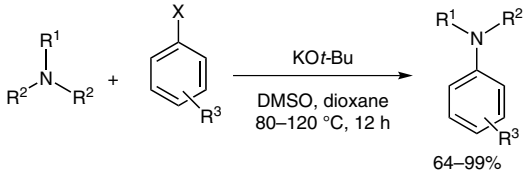

R^1 = Me, Et, Bu Ph, 4-Tol, 3-Tol, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-FC_6H_4
R^2 = Me, Et, Bu
R^3 = H, 4-Me, 3-Me, 2-Me, 4-F
X = I, Br, Cl

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Abstract A transition-metal-free, C–N bond-formation reaction between tertiary amines and aryl halides is reported. Under the optimal conditions, various aromatic and aliphatic tertiary amines react with aryl halides, including iodides, bromides, and chlorides, to give monoaminated products, *N*,*N*-dialkylanilines and *N*-alkyl-*N*-arylanilines, in good to high yields. Based on the experimental results, the reaction is believed to occur via an aryne intermediate derived from the aryl halide.

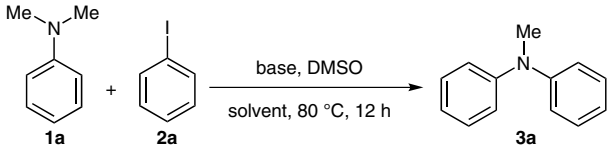
Key words transition-metal-free, tertiary amines, aryl halides, amination reaction, synthetic method

Arylamines, which can be frequently found in natural products as compounds with biological and pharmaceutical activity, are very interesting molecules in organic synthesis.[1] Recent syntheses of such compounds are the palladium-catalyzed Buchwald–Hartwig[2] and copper-catalyzed Ullmann couplings between primary or secondary amines and aryl halides.[3] However, the Buchwald–Hartwig coupling requires the use of expensive palladium complexes and the Ullmann couplings usually require excess of the copper salts and higher temperatures. In addition, transition-metal contaminants are commonly unavoidable, which is unacceptable, especially in pharmaceutical fine chemicals. These shortcomings have prompted the pursuit of transition-metal-free methods for the synthesis of arylamines. However, compared to numerous reports on transition-metal-catalyzed amination reactions, there are only a few reports of transition-metal-free couplings between primary or secondary amines and aryl halides.[4] In addition, transformations involving other electrophiles such as arylboronic acids and their derivatives,[5] *o*-silylaryl triflates,[6] and diaryliodonium salts[7] rather than aryl halides have also been developed. Among these electrophiles, aryl halides are the most desirable due to their easy availability and lower cost. However, to the best of our knowledge, only primary and secondary amines have been used as the nucleophile in the transition-metal-free amination of aryl halides, and there has been no report of the application of aromatic tertiary amines as nucleophiles to date.[8,9] In our continuing program to develop new methodologies for the formation of C–N bonds,[10] we found that both aromatic and aliphatic tertiary amines and aryl halides can be coupled mediated by potassium *tert*-butoxide and dimethyl sulfoxide in the absence of a transition metal. Herein, we report these results in detail.

At the outset of our investigation, a mixture of *N*,*N*-dimethylaniline (**1a**, 0. 55 mmol), iodobenzene (**2a**, 3.0 equiv), and dimethyl sulfoxide (3.0 equiv) in dioxane (0.9 mL) was stirred at 80 °C for 12 hours to evaluate the effects of various bases. Representative results are shown in Table 1. To our delight, using potassium *tert*-butoxide (4.0 equiv) as the base gave the desired C–N coupling product **3a** in 89% yield (entry 1).[11] However, other bases, such as lithium *tert*-butoxide, sodium *tert*-butoxide, sodium hydroxide, potassium hydroxide, potassium carbonate, cesium carbonate, potassium hydrogen carbonate, and tripotassium phosphate trihydrate, gave either very low yields of **3a** or no reaction was observed (entries 2–9). Subsequently, the conditions were further tuned using potassium *tert*-butoxide as the base. For example, decreasing the amount of potassium *tert*-butoxide from four to three equivalents gave a slight decrease in the yield of **3a** to 82% (entry 10). In addition, three equivalents of dimethyl sulfoxide were also found to be essential for this reaction. For instance, decreasing the amount of dimethyl sulfoxide from three to two equivalents or in the absence of dimethyl sulfoxide gave **3a** in only 73 and 23% yields, respectively (entries 11 and 12).[12] Furthermore, to achieve a satisfactory result, three equivalents of iodobenzene (**2a**) were also necessary. For example, using two equivalents of **2a** resulted in a drastically reduced yield of **3a** of 68% (entry 13). Furthermore, the use of a variety of

solvents was examined, and it was found that 1,2-dimethoxyethane, tetrahydrofuran, and toluene gave lower yields compared to dioxane (entries 1 and 14–16); dimethyl sulfoxide was also a suitable solvent giving **3a** in good yield (entry 17). However, further studies showed that dimethyl sulfoxide was unsuitable for other substrates tested. Thus, the optimized reaction conditions are those shown in Table 1, entry 1.[13]

Table 1 Optimization for the Reaction of *N*,*N*-Dimethylaniline (**1a**) with Iodobenzene (**2a**)

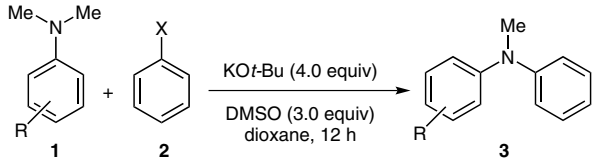


Entry[a]	Base	Solvent	Yield[b] (%)
1	KO*t*-Bu	dioxane	89
2	LiO*t*-Bu	dioxane	<5
3	NaO*t*-Bu	dioxane	<5
4	NaOH	dioxane	<5
5	KOH	dioxane	<5
6	K_2CO_3	dioxane	–[c]
7	Cs_2CO_3	dioxane	–[c]
8	$KHCO_3$	dioxane	–[c]
9	$K_3PO_4{\cdot}3H_2O$	dioxane	–[c]
10[d]	KO*t*-Bu	dioxane	82
11[e]	KO*t*-Bu	dioxane	73
12[f]	KO*t*-Bu	dioxane	23
13[g]	KO*t*-Bu	dioxane	68
14	KO*t*-Bu	DME	78
15	KO*t*-Bu	THF	75
16	KO*t*-Bu	toluene	63
17	KO*t*-Bu	DMSO	82

[a] Reaction conditions: **1a** (0.55 mmol), **2a** (3.0 equiv), base (4.0 equiv), DMSO (3.0 equiv), solvent (0.9 mL), 80 °C, 12 h.
[b] Isolated yields.
[c] Not reported.
[d] KO*t*-Bu (3.0 equiv) was used.
[e] DMSO (2.0 equiv) was used.
[f] No DMSO was added.
[g] **2a** (2.0 equiv) was used.

Under the optimal conditions, the reaction was first investigated using a variety of *N*,*N*-dimethylanilines **1** and halobenzenes **2**, such as iodobenzene (**2a**), bromobenzene (**2b**), and chlorobenzene (**2c**) as the substrate. As can be seen from Table 2, all reactions proceeded smoothly to give the desired aminated products **3a**–**f** in moderate to high yields. Substituents on the anilines did not affect the reactions significantly. For example, electron-rich substituents, such as 4-Me **1b**, 3-Me **1c**, and 4-OMe **1d**, electron-neutral **1a** and electron-poor groups, such as 4-F **1e**, are all tolerated to give products **3a**–**e** in good to high yields (entries 1–4, 6–10, and 12–14). Moderate yields can still be achieved when substrate **1f** bearing a sterically hindered 2-methoxy group was used as the substrate (entries 5 and 11). In addition, it seems that higher yields can be obtained if anilines bearing electron-rich substituents were used as the substrates. For instance, highest yields were observed when 4-methoxy-*N*,*N*-dimethylaniline (**1d**) was used (entries 3, 9, and 14). Halobenzenes also had some effect on the reactions. For example, for reactions involving bromobenzene (**2b**) and chlorobenzene (**2c**), higher temperatures (100 and 120 °C) are necessary to achieve satisfactory results (entries 6–14). It was worthy of noting here that with the increase of the electronegative of the halogen atoms, the reaction conditions became harsher. For example, the reactions involving iodides can be performed at 80 °C, while those of bromides and chlorides should be carried out at 100 and 120 °C, respectively. Based on these results, the conclusion may be drawn that aryl fluorides will not be good substrates in such transformations as harsher conditions, such as higher temperature or stronger base, will be necessary.

Table 2 Reactions of *N*,*N*-Dimethylanilines **1** with Halobenzenes **2**



Entry[a]	1	R	Halide	X	Temp (°C)	Product	Yield[b] (%)
1	**1b**	4-Me	**2a**	I	80	**3b**	91
2	**1c**	3-Me	**2a**	I	80	**3c**	91
3	**1d**	4-OMe	**2a**	I	80	**3d**	99
4	**1e**	4-F	**2a**	I	80	**3e**	83
5	**1f**	2-OMe	**2a**	I	80	**3f**	67
6	**1a**	H	**2b**	Br	100	**3a**	96
7	**1b**	4-Me	**2b**	Br	100	**3b**	94
8	**1c**	3-Me	**2b**	Br	100	**3c**	90
9	**1d**	4-OMe	**2b**	Br	100	**3d**	99
10	**1e**	4-F	**2b**	Br	100	**3e**	84
11	**1f**	2-OMe	**2b**	Br	100	**3f**	70
12	**1b**	4-Me	**2c**	Cl	120	**3b**	83
13	**1c**	3-Me	**2c**	Cl	120	**3c**	72
14	**1d**	4-OMe	**2c**	Cl	120	**3d**	93

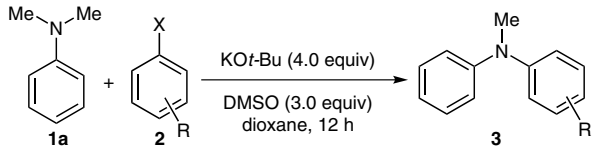
[a] Reaction conditions: **1** (0.55 mmol), **2** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 12 h.
[b] Isolated yields.

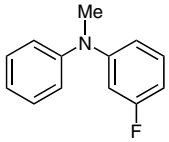
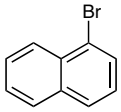
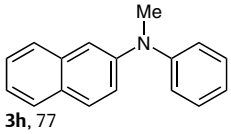
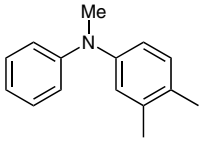
Encouraged by these results, the reactions of *N*,*N*-dimethylaniline (**1a**) with various aryl halides **2** bearing electron-poor, electron-rich, and sterically hindered substituents were also examined under the optimal conditions. It seems that the structure of the aryl halide **2** also has some effect on these reactions. For instance, the desired C–N coupling products can be obtained in moderate to high yields for all the reactions investigated (Table 3). However, the steric and electronic effects of the substituents on the aryl halides will result in different regioselective aminated products **3**.[14] Based on the results shown in Table 3, the conclusion can be drawn that the direct C–N coupling between aromatic tertiary amines and aryl halides takes place via aryne intermediates.[15] Based on this assumption, the steric and electronic effect of the substituents on the aryl halides can thus be explained. For example, the reactions of *N*,*N*-dimethylaniline (**1a)** with 4-iodotoluene (**2d**) and 3-iodotoluene (**2e**) give a mixture of *para*- and *meta*-aminated products **3b** and **3c** in both cases (entries 1 and 2), implying that the same aryne intermediate was formed. For the reaction of sterically hindered 2-bromotoluene (**2g**), only the *meta*-aminated product **3c** is isolated in 64% yield (entry 4), probably due to the steric effect of the methyl group on the aryne intermediate formed, which thus resulted in solely in *meta*-amination.

Furthermore, the reactions of 4-methoxy-*N*,*N*-dimethylaniline (**1d**) with 4-, 3-, or 2-chlorotoluenes **2m**–**o** were also investigated under the optimal conditions. As can be seen from Table 4, all reactions took place to give the desired aminated products in good to almost quantitative yields. For the reactions involving 4-chlorotoluene (**2m**) and 3-chlorotoluene (**2n**), the *para*- and *meta*-aminated products **3j** and **3k** were both obtained in very high yields, respectively, perhaps due to the same aryne intermediate being formed in both cases (Table 4, entries 1 and 2). For the reaction involving 2-chlorotoluene (**2o**), only the *meta*-aminated product **3k** was obtained in 80% yield (entry 3), similarly due to the steric hindrance of the aryne intermediate formed.

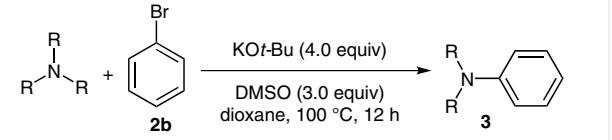
The transition-metal-free amination of aliphatic tertiary amines such as triethylamine (**1g**) and tributylamine (**1h**) with bromobenzene (**2b**) was also examined. As can be seen from Scheme 1, both reactions proceeded well under the optimal conditions to give the desired aminated products **3l** and **3m**, respectively, in good yields. Therefore, compared to the previously reported methods, which were limited to the reactions of aromatic or aliphatic tertiary amines, respectively,[8,9] both aromatic and aliphatic tertiary amines can be tolerated in this method, implying its broader substrate compatibility.

Table 3 Reactions of *N*,*N*-Dimethylaniline (**1a**) with Aryl Halides **2**



Entry[a]	2	R	X	Temp (°C)	Yield[b] (%)	
1[c]	**2d**	4-Me	I	80	**3b**, 36	**3c**, 38
2[c]	**2e**	3-Me	I	100	**3b**, 27	**3c**, 43
3	**2f**	4-F	I	120	**3e**, 82	 **3g**, 17
4	**2g**	2-Me	Br	100	**3c**, 64	
5[c]	**2h**	4-Me	Br	100	**3b**, 48	**3c**, 45
6[c]	**2i**	3-Me	Br	100	**3b**, 31	**3c**, 53
7	 **2j**			100	 **3h**, 77	
8	**2k**	4-F	Br	100	**3e**, 82	**3g**, 12
9	**2l**	3,4-Me_2	Br	100	 **3i**, 65	

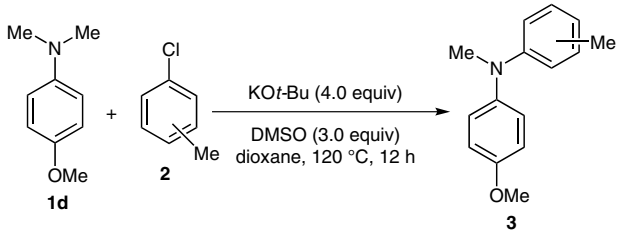
[a] Reaction conditions: **1a** (0.55 mmol), **2** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 12 h.
[b] Isolated yields.
[c] Mixture of **3b** and **3c** was obtained after flash column chromatography (see Supporting Information for details).

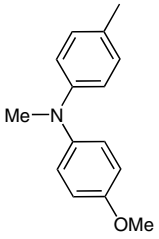
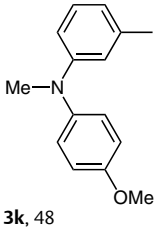


Scheme 1 Reactions of aliphatic tertiary amines with bromobenzene. *Reagents and conditions*: **1** (0.55 mmol), **2b** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 100 °C, 12 h.

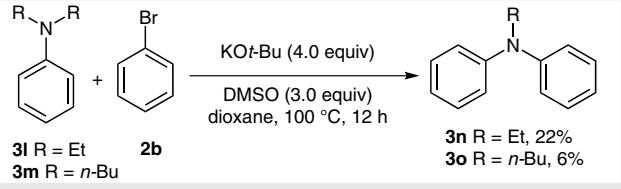
It should be noted that in these reactions no diarylated amines were isolated by column chromatography. In addition, it was indeed found that the above products **3l** and **3m** were not suitable substrates in the reaction with bromobenzene under the optimal conditions and predominantly the unreacted starting materials were recovered (Scheme 2).

Table 4 Reactions of 4-Methoxy-*N*,*N*-dimethylaniline (**1d**) with Chlorotoluenes **2m–o**



Entry[a]	2	Substitution	Yield[b] (%)	
1[c]	**2m**	4-Me	 **3j**, 51	 **3k**, 48
2[c]	**2n**	3-Me	**3j**, 37	**3k**, 55
3	**2o**	2-Me	**3k**, 80	

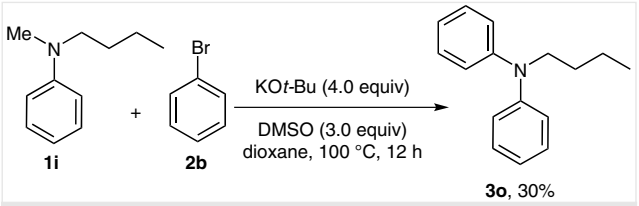
[a] Reactions conditions: **1d** (0.55 mmol), **2** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 120 °C, 12 h.
[b] Isolated yields.
[c] A mixture of **3j** and **3k** was obtained after flash column chromatography (see Supporting Information for details).



Scheme 2 Reactions of *N*,*N*-diethylaniline and *N*,*N*-dibutylaniline with bromobenzene. *Reagents and conditions*: **3l** or **3m** (0.55 mmol), **2b** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 100 °C, 12 h.

Furthermore, the reaction of *N*-butyl-*N*-methylaniline (**1l**) with bromobenzene (**2b**) was also carried out under the optimal conditions. In this case, only the demethylated product **3o** was isolated in 30% yield, and most of the starting aniline was recovered, suggesting that in such transformations only the CH_3–N bond is cleaved (Scheme 3).

In conclusion, we have developed a facile and convenient C–N coupling of aromatic and aliphatic tertiary amines with aryl halides. It may be worthy of note here that this is the first example of such a transformation between aromatic tertiary amines and aryl halides in the absence of any transition metals. A variety of aromatic and aliphatic tertiary amines and aryl halides are tolerated to give the desired aminated products in moderate to high yields. Based



Scheme 3 Reaction of *N*-butyl-*N*-methylaniline with bromobenzene. *Reagents and conditions*: **1i** (0.55 mmol), **2b** (3.0 equiv), KO*t*-Bu (4.0 equiv), DMSO (3.0 equiv), dioxane (0.9 mL), 100 °C, 12 h.

on the experiments, the reaction is believed to occur via aryne intermediates derived from aryl halides. Efforts are underway to expand this methodology toward other reactions rather than just C–N coupling.

NMR spectra were recorded at 500 (for ^{1}H NMR) and 125 MHz (for ^{13}C NMR), respectively. ^{1}H NMR and ^{13}C NMR spectra recorded in $CDCl_3$ solutions were referenced to TMS (δ = 0.00 ppm) and the residual solvent peak (δ = 77.0 ppm), respectively. Organic solvents used were dried by standard methods. Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel.

Amination between Tertiary Amines and Aryl Halides; General Procedure

Under an atmosphere of N_2, KO*t*-Bu (2.2 mmol), dioxane (0.9 mL), DMSO (1.65 mmol), tertiary amine **1** (0.55 mmol), and aryl halide **2** (1.65 mmol) were successively added to a Schlenk reaction tube. The mixture was stirred vigorously at 80–120 °C for 12 h. Then the mixture was diluted with EtOAc, washed with sat. brine, and dried (anhyd Na_2SO_4). Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether and petroleum ether–EtOAc, 100:1 for the methoxy group derived products) to give pure products **3**.

N-Methyldiphenylamine (3a)[10f]

Colorless liquid; yield: 89.6 mg (89%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.25 (t, *J* = 8.0 Hz, 4 H), 7.01 (d, *J* = 8.0 Hz, 4 H), 6.93 (t, *J* = 8.0 Hz, 2 H), 3.29 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.0, 129.1, 121.2, 120.4, 40.2.

N,4-Dimethyl-*N*-phenylaniline (3b)[16]

Colorless liquid; yield: 98.6 mg (91%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.22 (t, *J* = 7.5 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 7.5 Hz, 2 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 3.28 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.3, 146.6, 132.0, 129.9, 129.0, 122.5, 119.8, 118.2, 40.3, 20.7.

N,3-Dimethyl-*N*-phenylaniline (3c)[17]

Colorless liquid; yield: 98.9 mg (91%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.24 (t, *J* = 8.5 Hz, 2 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 6.98 (d, *J* = 8.5 Hz, 2 H), 6.91 (t, *J* = 7.5 Hz, 1 H), 6.84–6.82 (m, 2 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 3.27 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.1, 149.0, 138.9, 129.1, 129.0, 122.3, 121.4, 120.9, 120.1, 117.9, 40.2, 21.5.

4-Methoxy-*N*-methyl-*N*-phenylaniline (3d)[16]

Colorless liquid; yield: 116.0 mg (99%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.19 (dd, *J* = 9.0, 7.0 Hz, 2 H), 7.08 (d, *J* = 9.0 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 6.79–6.76 (m, 3 H), 3.80 (s, 3 H), 3.25 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3, 149.8, 142.3, 128.9, 126.1, 118.4, 115.8, 114.8, 55.5, 40.4.

4-Fluoro-*N*-methyl-*N*-phenylaniline (3e)[16]

Colorless liquid; yield: 91.7 mg (83%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.24–7.21 (m, 2 H), 7.04–6.96 (m, 4 H), 6.88–6.85 (m, 3 H), 3.25 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6 (d, J_{C-F} = 240.3 Hz), 149.2, 145.1, 129.1, 124.2 (d, J_{C-F} = 7.9 Hz), 120.0, 117.9, 115.9 (d, J_{C-F} = 22.1 Hz), 40.5.

2-Methoxy-*N*-methyl-*N*-phenylaniline (3f)[18]

Colorless liquid; yield: 78.5 mg (67%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.24–7.14 (m, 4 H), 6.99–6.94 (m, 2 H), 6.71 (t, *J* = 7.5 Hz, 1 H), 6.65 (dd, *J* = 9.0, 1.0 Hz, 2 H), 3.76 (s, 3 H), 3.21 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 149.3, 136.7, 129.1, 128.7, 126.9, 121.2, 117.1, 113.4, 112.6, 55.6, 39.0.

3-Fluoro-*N*-methyl-*N*-phenylaniline (3g)

Colorless liquid; yield: 18.8 mg (17%).

IR (neat): 3060, 2875, 2822, 2352, 1613, 1587, 1491, 1348, 1259, 1186, 1152, 1123, 1027, 995, 952, 939, 833, 755, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.35–7.31 (m, 2 H), 7.12–7.07 (m, 4 H), 6.65–6.63 (m, 1 H), 6.59–6.56 (m, 1 H), 6.56–6.51 (m, 1 H), 3.29 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.7 (d, J_{C-F} = 242.1 Hz), 150.84, 150.76, 148.3, 129.9 (d, J_{C-F} = 9.9 Hz), 129.5, 123.7 (d, J_{C-F} = 5.1 Hz), 112.8, 105.9 (d, J_{C-F} = 21.4 Hz), 104.1 (d, J_{C-F} = 24.9 Hz), 40.2.

MS (ESI): *m*/*z* = 202 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{13}FN$: 202.1027; found: 202.1020.

***N*-Methyl-*N*-phenylnaphthalen-2-amine (3h)**[9]

Colorless liquid; yield: 98.7 mg (77%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.73–7.65 (m, 3 H), 7.41–7.38 (m, 1 H), 7.34–7.27 (m, 4 H), 7.20 (dd, *J* = 9.0, 7.5 Hz, 1 H), 7.10 (d, *J* = 7.5 Hz, 2 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 3.40 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 146.4, 134.6, 129.3, 129.1, 128.6, 127.5, 126.7, 126.2, 123.8, 122.0, 121.7, 121.4, 114.6, 40.7.

***N*,3,4-Trimethyl-*N*-phenylaniline (3i)**[9]

Colorless liquid; yield: 75.5 mg (65%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.22 (t, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 6.92–6.90 (m, 3 H), 6.86–6.83 (m, 2 H), 3.27 (s, 3 H), 2.23 (s, 3 H), 2.22 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.3, 146.8, 137.5, 131.0, 130.4, 128.9, 124.1, 120.3, 119.5, 117.8, 40.3, 19.9, 19.1.

4-Methoxy-*N*-methyl-*N*-(4-tolyl)aniline (3j) and 4-Methoxy-*N*-methyl-*N*-(3-tolyl)aniline (3k)

Inseparable mixture; colorless liquid; yield: 123.6 mg (99%).

IR (neat): 3040, 2994, 2934, 2822, 2802, 2597, 1577, 1507, 1461, 1438, 1334, 1235, 1175, 1126, 1036, 917, 836, 766, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (**3j**) = 7.01 (d, *J* = 8.0 Hz, 4 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 3.77 (s, 3 H), 3.21 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (**3j**) = 155.5, 147.5, 142.8, 129.5, 128.5, 124.5, 117.4, 114.7, 55.4, 40.5, 20.4.

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (**3k**) = 7.09–7.05 (m, 3 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 6.61–6.59 (m, 3 H), 3.78 (s, 3 H), 3.22 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (**3k**) = 156.1, 149.8, 142.3, 138.6, 128.7, 126.0, 119.4, 116.6, 114.6, 113.1, 55.4, 40.6, 21.7.

MS (ESI): *m*/*z* = 228 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{18}NO$: 228.1383; found: 228.1379.

4-Methoxy-*N*-methyl-*N*-(2-tolyl)aniline (3k)

Colorless liquid; yield: 100.0 mg (80%).

IR (neat): 3033, 2835, 1603, 1580, 1511, 1487, 1338, 1239, 1179, 1033, 915, 833, 768, 692 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.09–7.06 (m, 3 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 6.61–6.59 (m, 3 H), 3.78 (s, 3 H), 3.22 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 149.7, 142.2, 138.6, 128.7, 126.0, 119.3, 116.4, 114.6, 113.0, 55.4, 40.5, 21.7.

MS (ESI) : *m*/*z* = 228 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{18}NO$: 228.1383; found: 228.1386.

***N*,*N*-Diethylaniline (3l)**[19]

Yellow liquid; yield: 68.8 mg (84%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.20 (t, *J* = 7.5 Hz, 2 H), 6.67 (d, *J* = 7.5 Hz, 2 H), 6.63 (t, *J* = 7.5 Hz, 1 H), 3.24 (q, *J* = 7.0 Hz, 4 H), 1.14 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.7, 129.2, 115.3, 111.8, 44.2, 12.5.

***N*,*N*-Dibutylaniline (3m)**[20]

Yellow liquid; yield: 86.8 mg (77%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.19 (dd, *J* = 9.0, 7.5 Hz, 2 H), 6.65–6.60 (m, 3 H), 3.25 (t, *J* = 7.5 Hz, 4 H), 1.58–1.53 (m, 4 H), 1.38–1.31 (m, 4 H), 0.95 (t, *J* = 7.5 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.2, 129.1, 115.1, 111.7, 50.7, 29.4, 20.3, 14.0.

***N*-Ethyldiphenylamine (3n)**[21]

Pale yellow liquid; yield: 23.8 mg (22%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.27–7.24 (m, 4 H), 7.00–6.98 (m, 4 H), 6.95–6.92 (m, 2 H), 3.77 (q, *J* = 7.0 Hz, 2 H), 1.22 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.7, 129.2, 121.1, 120.9, 46.4, 12.7.

***N*-Butyldiphenylamine (3o)**[22]

Pale yellow liquid; yield: 37.1 mg (30%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.25–7.21 (m, 4 H), 6.98–6.97 (m, 4 H), 6.93–6.90 (m, 2 H), 3.67 (t, *J* = 7.5 Hz, 2 H), 1.67–1.61 (m, 2 H), 1.39–1.31 (m, 2 H), 0.91 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.1, 129.2, 121.0, 120.9, 52.1, 29.6, 20.3, 13.9.

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Supporting Information

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